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Preparation of Layered Diacetylenes as a Demonstration of Strategies for Supramolecular Synthesis

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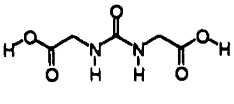
The physical and chemical properties of a molecular solid depend directly upon the relative orientations and spacings of the constituent molecules. Unfortunately, it is very difficult to control molecular orientation and spacing in a crystal. Many groups,[1] including our own,[2] have tried to approach the problem by combining methods of traditional molecular synthesis with the techniques of supramolecular synthesis.[3]

In previous studies[2] we have used substituted ureas and vinylogous ureas to prepare a variety of layered organic crystals.[4] The urea functionality consistently forms one-dimensional hydrogen-bonded α-networks[5] via hydrogen bonds between the carbonyl of one urea and the anti-hydrogen atoms of the nitrogen atoms of a neighboring urea. If substituents, such as carboxylic acid functionalities, are added to the urea, the one-dimensional α-networks can be brought together to form a two-dimensional β-network. By choosing the appropriate molecule, we have been able to control the spacing[6] and symmetry of the hydrogen-bonded β-networks that define these layers. Having identified and demonstrated successful strategies for the supramolecular synthesis of specific layered structures, we now report an application of these strategies in the field of solid state reactions.

It is well-known that various substituted diacetylenes polymerize in the solid state.[7] The polymerization process is a topochemical one, occurring only if the molecules are properly aligned at a critical repeat distance near 5.0 Å and with an orientation angle of about 45° relative to the translation axis. Since this distance is similar to the repeat distance found in the layered ureylene dicarboxylic acids we studied previously, this class of compounds is a potential candidate for the preparation of layered diacetylenes with the topochemical conditions necessary for polymerization.

Two fundamentally different approaches to the layered diacetylene goal can be envisioned using the strategies we have developed for layer synthesis. The obvious and more traditional solution would be to prepare an appropriate urea with a diacetylene functionality and additional substituents that will lead to a β-network.[8] A disadvantage of this linear strategy, using a *single* molecule, is the complexity of the molecular synthesis that may be required.

For a second solution to this problem we have explored a host–guest/cocrystal approach. This strategy requires the design of *two* different molecules that will together contain the components needed for the self-assembly of the β-network and the diacetylene functionality.[9,10] One molecule will contain a substituted urea that will control the critical intermolecular spacing and will serve as a host for the second molecule, the diacetylene guest.[11] The remaining required design element is an appropriate set of matched substituents that will assure a strong intermolecular interaction between these two molecules. In our initial designs we have used the strong pyridine–carboxylic acid hydrogen bond to direct this important intermolecular association.[12,13]



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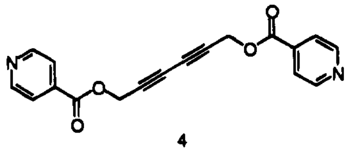

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To evaluate this strategy, we prepared the ureylene dicarboxylic acid, **1**, and allowed the compound to form cocrystals with 4,4′-bipyridyl, **2**, and with 1,2-bis(4-pyridyl)ethane, **3**. X-ray diffraction studies of each cocrystal confirmed the formation of the expected β-network structure.[14] The β-network of the **1**–**2** cocrystal is shown in Figure 1. The layer structure of the **1**–**3** cocrystal is similar.[15]

Encouraged by the success of these experiments, we prepared a pyridyl-substituted diacetylene **4**[16] and allowed it to form a

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(1) (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (b) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312. (c) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37. (d) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696.

(2) (a) Zhao, X.; Chang, Y.-L.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 6627. (b) Chang, Y.-L.; West, M. A.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5991. (c) Toledo, L. M.; Lauher, J. W.; Fowler, F. W. *Chem. Mater.* **1994**, *6*, 1222–1226.

(3) The application of intermolecular interactions such as hydrogen bonding for the preparation of supramolecular structures. (a) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. Etter, M. C. *J. Phys. Chem.* **1991**, *95*, 4601. (b) Aakeröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, 397–407. (c) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383–2420.

(4) For other recent approaches to the preparation of layered structures, see: (a) Hollingsworth, M. D.; Brown, M. E.; Santarsiero, B. D.; Huffman, J. C.; Goss, C. R. *Chem. Mater.* **1994**, *6*, 1227–1244. (b) Russell, V. A.; Etter, M. C.; Ward, M. D. *Chem. Mater.* **1994**. *6*, 1206–1217. (c) Aakeröy, C. B.; Nieuwenhuyzen, M. *J. Am. Chem. Soc.* **1994**, *116*, 10983–10991.

(5) The α- and β-networks are supramolecular structural features possessing translational symmetry in one and two directions, respectively. These networks, together with discrete assemblies and γ-networks, represent the four fundamental supramolecular structures. These terms are discussed further in ref 2a.

(6) A urea gives a characteristic spacing of 4.6 Å. This spacing can be varied by changing the functional group. Vinylogous ureas give spacings of 6.7 Å, and oxamides give spacings of 5.0 Å; see ref 2c.

(7) (a) Bloor, D., Chance, R. R., Eds. *Polydiacetylenes: Synthesis, Structure and Electronic Properties*; Martinus Nijhoff: Dordrecht, The Netherlands, 1986. (b) Enkelmann, V. *Adv. Polym. Sci.* **1984**, *63*, 91.

(8) Diacetylenes containing the urea functionality have been synthesized and are known to polymerize. Prezicsi, A. F.; Prusik, T. Acid Complexed Acetylenic Compounds useful as Environmental Indicating Materials. U.S. Patent Number 4,789,637, 1988.

(9) (a) *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: Oxford, 1991; Vol. 4. (b) *Molecular Inclusion and Molecular Recognition—Clathrates I*, Weber, E., Ed.; Topics in Current Chemistry 140; Springer-Verlag: Berlin, 1987. (c) *Molecular Inclusion and Molecular Recognition—Clathrates II*; Weber, E., Ed.; Topics in Current Chemistry 149; Springer-Verlag: Berlin, 1988.

(10) Many descriptors have been used to describe the various ordered arrangements of more than one molecule in the solid state. Among these are cocrystals, mixed crystals, host–guest compounds, clathrates, inclusion compounds, etc. See ref 9b, p 3.

(11) In a related manner the topochemistry of a butadiene polymerization has been controlled by use of a perovskite-type layer structure. Tieke, B.; Chapuis, G. *Mol. Cryst. Liq. Cryst.* **1986**, *137*, 101–116.

(12) (a) Dega-Szafran, Z.; Dulewicz, E. *Org. Magn. Reson.* **1981**, *16*, 214–219. (b) Johnson, S. L.; Rumon, K. A. *J. Phys. Chem.* **1965**, *69*, 74–86. (c) Zeegers-Huyskens, T.; Sobczyk, L. *J. Mol. Liq.* **1990**, *46*, 263–284.

(13) The pyridine–carboxylic acid interaction has been previously used to organize molecules in polymer blends (Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954) and liquid crystals (Kato, T.; Fukumasa, M.; Fréchet, J. M. J. *Chem. Mater.* **1995**, *7*, 368).

(14) Crystal data: **1**–**2** cocrystal, a = 16.787(4) Å, b = 4.640(1) Å, c = 19.962(2) Å, β = 98.57(2)°, monoclinic $C2/c$, Z = 4, R = 0.040, R_w = 0.038 for 420 independent reflections with $F_o^2 > 3\sigma(F_o^2)$; **1**–**3** cocrystal, a = 19.991(5) Å, b = 9.593(2) Å, c = 9.275(6) Å, β = 91.32(2)°, monoclinic $P2_1/c$, Z = 4, R = 0.062, R_w = 0.081 for 1666 independent reflections; **1**–**4** cocrystal, a = 27.061(7) Å, b = 4.706(6) Å, c = 18.077(8) Å, β = 90.21(7)°, monoclinic $C2/c$, Z = 4, R = 0.049, R_w = 0.057 for 916 independent reflections; **5**–**6** cocrystal, a = 24.124(5) Å, b = 4.631(4) Å, c = 21.984(8) Å, β = 102.69(4)°, monoclinic $P2/c$, Z = 4, R = 0.036, R_w = 0.038 for 1627 independent reflections; compound **4**, a = 7.892(3) Å, b = 8.554(4) Å, c = 12.733(6) Å, α = 101.54(2)°, β = 98.88(2)°, γ = 110.33(2)°, triclinic $P\bar{1}$, Z = 2, R = 0.035, R_w = 0.046 for 2108 independent reflections.

(15) Hollingsworth has also reported layered structures based upon the cocrystallization of urea and various dinitriles. See ref 4a.

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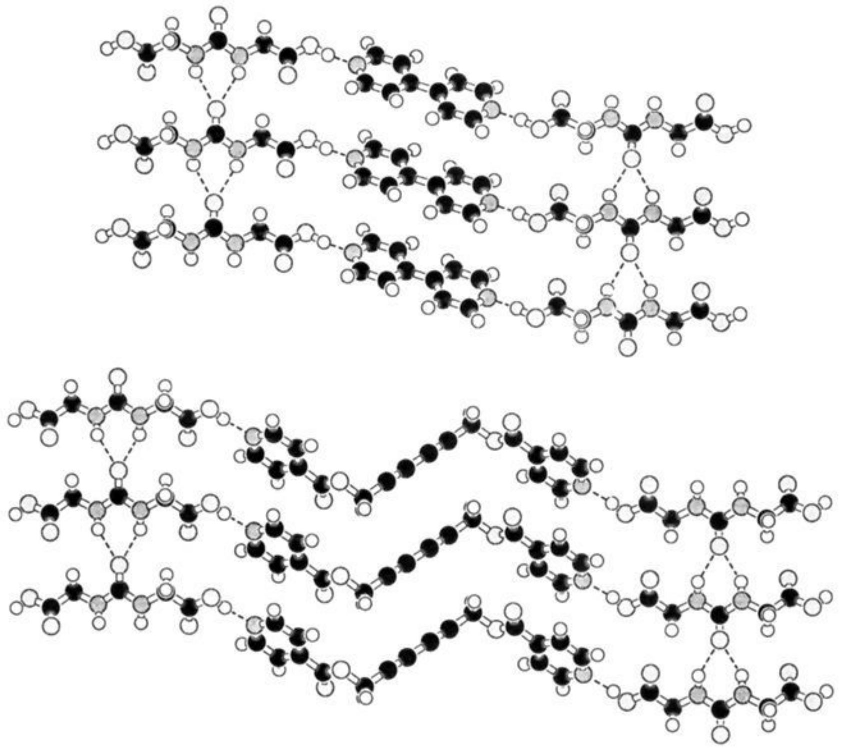
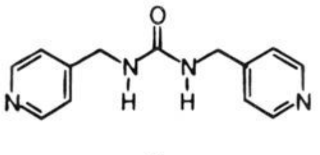


Figure 1. The layered structures of the **1**−**2** (top) and **1**−**4** (bottom) cocrystals. In the **1**−**4** cocrystal the spacing between adjacent diacetylene molecules is 4.71 Å with their main chains oriented at an angle of 56.3° relative to the translation axis.

cocrystal with **1**. In agreement with the design, the diacetylene functionalities have a spacing of 4.71 Å with their main chains oriented at an angle of 56.3° relative to the translation axis (Figure 1). This spacing and orientation are in accordance with the values needed for a successful polymerization.

As a further demonstration of the versatility of the above strategy, an alternate approach to a layered β-network of diacetylenes was explored. Urea **5**[17] and diyne **6** possess the correct functionalities to form a layered diacetylene β-network. The **5**−**6** cocrystal was prepared, and the X-ray diffraction studies of the cocrystal featured a layered β-network with a spacing of 4.63 Å between the diacetylene units with an orientation angle of 61.0°.[18]

The host−guest/cocrystal approach to supramolecular synthesis has many advantages over the single molecule approach.



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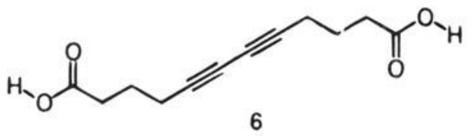

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The molecules required for the cocrystal approach will likely be less complex, and the molecular synthesis may be less demanding. With a flexible host like the substituted ureylenes an unlimited number of host variations can be made easily. This allows one to "fine-tune" the crystal environment of the guest. The spacing and the symmetry (including the chirality) of the lattice are subject to control. If one host environment proves to be unsuitable for a given guest, an alternate host can be selected for the same guest.

Although we have presented a strategy for controlling the topochemical reaction of diacetylenes, we close by emphasizing the generality of the host−guest/cocrystal concept. One molecule serves as the host and is used to control structure; a second, the guest, provides the function (optical, electrical, chemical, or physical). The strategy features a combination of molecular and supramolecular synthesis whose efficiency is due to its convergence at the supramolecular step.

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Supporting Information Available: Tables of crystal data, isotropic and anisotropic temperature factors, bond distances, angles, and intermolecular contacts (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(16) Dipyridine **4**, mp 119−120 °C, was prepared in 52% yield by coupling of propargyl nicotinate (Inoyatov, Sh.; Amanov, N. A.; Makhsumov, A. G.; Abdullaev, Sh. U. *Probl. Gig. Organ. Zdravookhr. Uzb.* **1976**, *5*, 85−8; *Chem. Abstr.* 90:162162q) using the Hay procedure (Jones, G. E.; Kendrick, D. A.; Holmes, A. B. *Org. Synth.* **1987**, *65*, 52−60).

(17) Urea **5** (mp 182−183 °C) was prepared in 76% yield from the commercially available 4-(aminomethyl)pyridine and triphosgene (Aldrich) in methylene chloride using triethylamine as a base. The diacetylene **6** is commercially available (Farchan Laboratories).

(18) Preliminary studies indicate a ready thermal polymerization of the diacetylenes in both the **1**−**4** and the **5**−**6** layered structures; both cocrystals turn blue, then black, upon heating, cocrystal **1**−**4** most readily. Among the important aspects of this unusual strategy for the preparation of supramolecular structures is that it can produce unusual polydiacetylenes and can be used to polymerize diacetylenes which by themselves, because of improper topochemistry, are unreactive. This the case with **4**; an X-ray structure shows that it lacks the necessary topochemistry for polymerization, and the pure compound does not polymerize. However, in the **1**−**4** cocrystal the proper topochemistry is present and a polymerization of **4** takes place. Each of the diacetylene polymers becomes a guest within a matrix of small molecule hosts. The ability to alter the structure of the host allows for the preparation of diacetylenes whose electrical and optical properties can be altered by the host and for the study of the polymerization process as a function of host structure. Also, it should be possible to remove the host with a suitable solvent producing the pure polydiacetylene.